SIGNIFICANCE OF DISSOLVED AND PARTICULATE METAL AND HYDROCARBON DETERMINATIONS IN URBAN RUNOFF SAMPLES

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ABSTRACT

The objectives of this paper are (i) to present reliable methods of quantification of both hydrocarbons and metals in dissolved and particulate urban runoff samples as well as atmospheric deposits, (ii) to emphasise on the validation procedure of these methods by using replicates, available certified samples or standard mixtures. NIST 1648 (urban particulate matter), BCR 144 R and 146 R (trace elements in sewage sludge from domestic and industrial origin, respectively), NIST 1643c (trace elements in water), SPS-WW1 and SPS-SW2 (waste and surface waters, respectively), were used with success for validating metal extraction and analysis procedures. In the absence of certified urban runoff sample for particulate or dissolved aliphatic hydrocarbons, NIST SRM 1941a was used as noncertified particulate sample (marine sediment certified only for aromatic hydrocarbons) and Florida TPH mix (NSI Environmental Solutions) as a mixture of 17 dissolved aliphatic hydrocarbons from C_{10} to C_{40}. Such validation procedures enable a better discrimination between sample heterogeneity and determination precision.

KEYWORDS

Hydrocarbon, metal, determination, validation, urban runoff, sampling.

INTRODUCTION.

Since 1996, an experimental catchment area has been set up by the Cereve in the centre of Paris (France) in order to study urban storm water from the atmosphere to the combined sewer outlet (Chebbo *et al.*, 1999). Briefly, this catchment covers an area of 42 ha, densely populated (295 inhabitants.ha^{-1}) and is impervious at 90%. This catchment can be divided into three kinds of urban surfaces, leading to three different types of runoff: roofs cover 54.5% of the area, streets represent 23%, and the remaining 22.5% of the surface takes in courtyards, gardens and public areas. The experiments carried out in this catchment were based on the characterisation of the different types of urban runoff from a town centre including a combined drainage network. Many parameters have been measured including micropollutants such as hydrocarbons (aromatic and aliphatic hydrocarbons) and metals (Cu, Zn, Pb, Cd) (Chebbo *et al.*, 1999).

Quantitative analysis of such individual pollutants at trace levels, i.e. metals and hydrocarbons, still present many difficulties especially when one takes into account spatial and temporal heterogeneity of samples. Therefore analysts have to validate the whole procedure, from the sampling to the analysis itself, in order to get reliable data. During the last ten years, the accuracy and precision of such measurements have increased. At the same time, detection limits have tremendously decreased. Improvements in procedures for extraction, purification and quantification have been achieved (Baumard and Budzinski, 1997a, b).

The reproducibility of a method can be estimated with the replicate analysis of a homogeneous sample. However, the systematic bias of the system, i.e. the accuracy of the analytical procedure, can be estimated by

analysing certified reference material that has been well characterised and is similar in structure and contamination with actual samples.

The analytical procedures developed for the analysis of hydrocarbons and metals have several objectives. Firstly, it is important to obtain an extract, free of most of the interfering compounds. Secondly, the absolute losses of compound (for all the different steps of the protocol) are estimated. Finally the whole protocol is validated resulting in an optimised reproducibility for the analytical procedure and the best recoveries for the compounds studied.

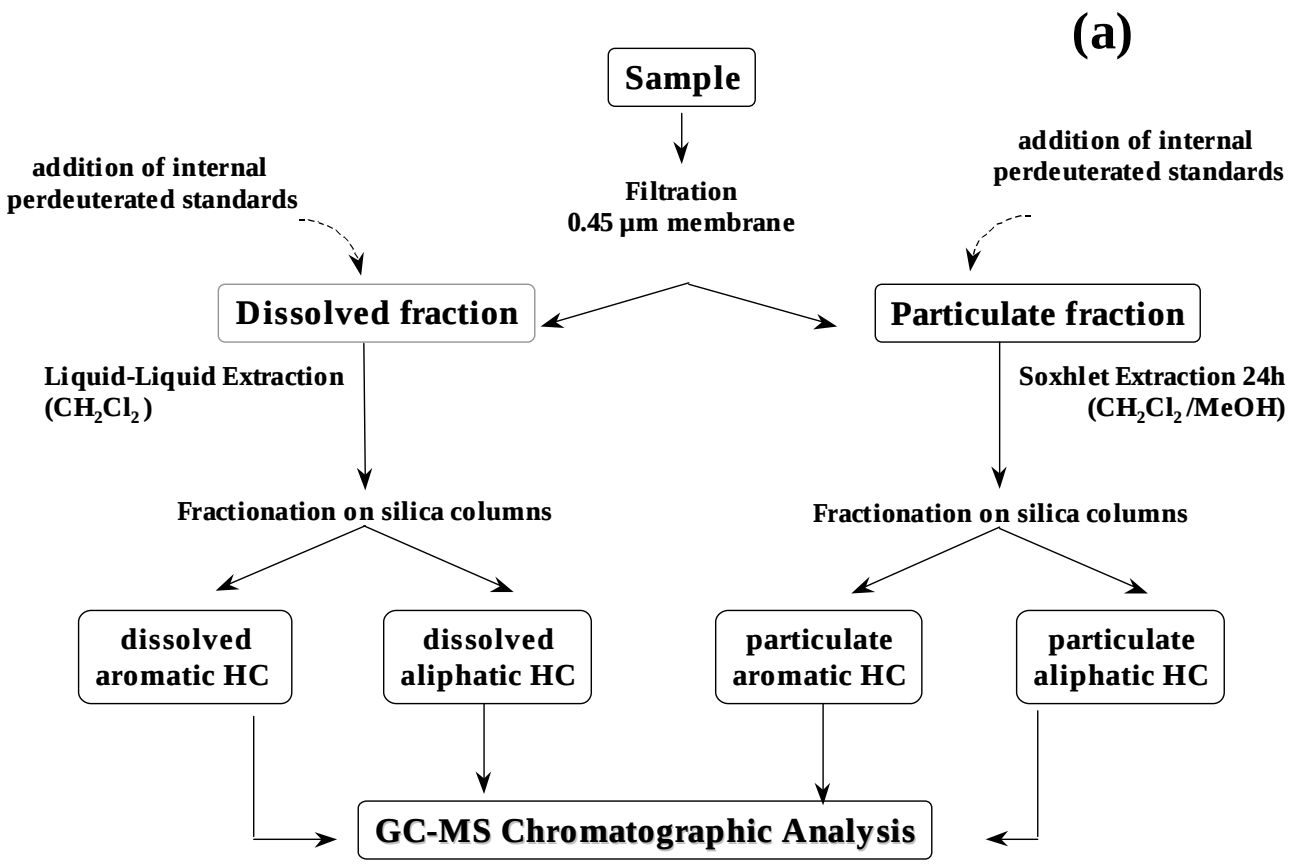
MATERIAL AND METHODS

Sampling strategy in the experimental urban catchment

The experiments carried out in this catchment were based on the characterisation of different types of urban runoff from a town centre (atmospheric deposit, roof, road and yard runoff, dry and wet weather waste water), in 1996 and 1997, which were collected for assessing the sources and evolution of pollutants during their transport within urban catchment. Sampling procedures for urban runoff within the experimental urban catchment “Le Marais” have been previously described (Gromaire-Mertz *et al*., 1998a, b).

Processing of samples

To avoid contamination of the sample the vessels used for sampling were treated as follows : (i) for hydrocarbons, glassware was cleaned with 5 % Decon detergent (Prolabo) and water, rinsed with purified water (Milli-Ro 5 Plus, Millipore), calcinated in an oven at 450°C for 2h and then rinsed with acetone, solvents were purified by distillation, (ii) for metals, polyethylene or Teflon vessels were soaked for 24h in 2 % Extran detergent (Merck) and 24h in 10 % nitric acid baths, then thoroughly rinsed with ultrapure water (Milli-Q Plus 185, Millipore) before drying in a laminar flow hood, inside a class 1000 clean room.



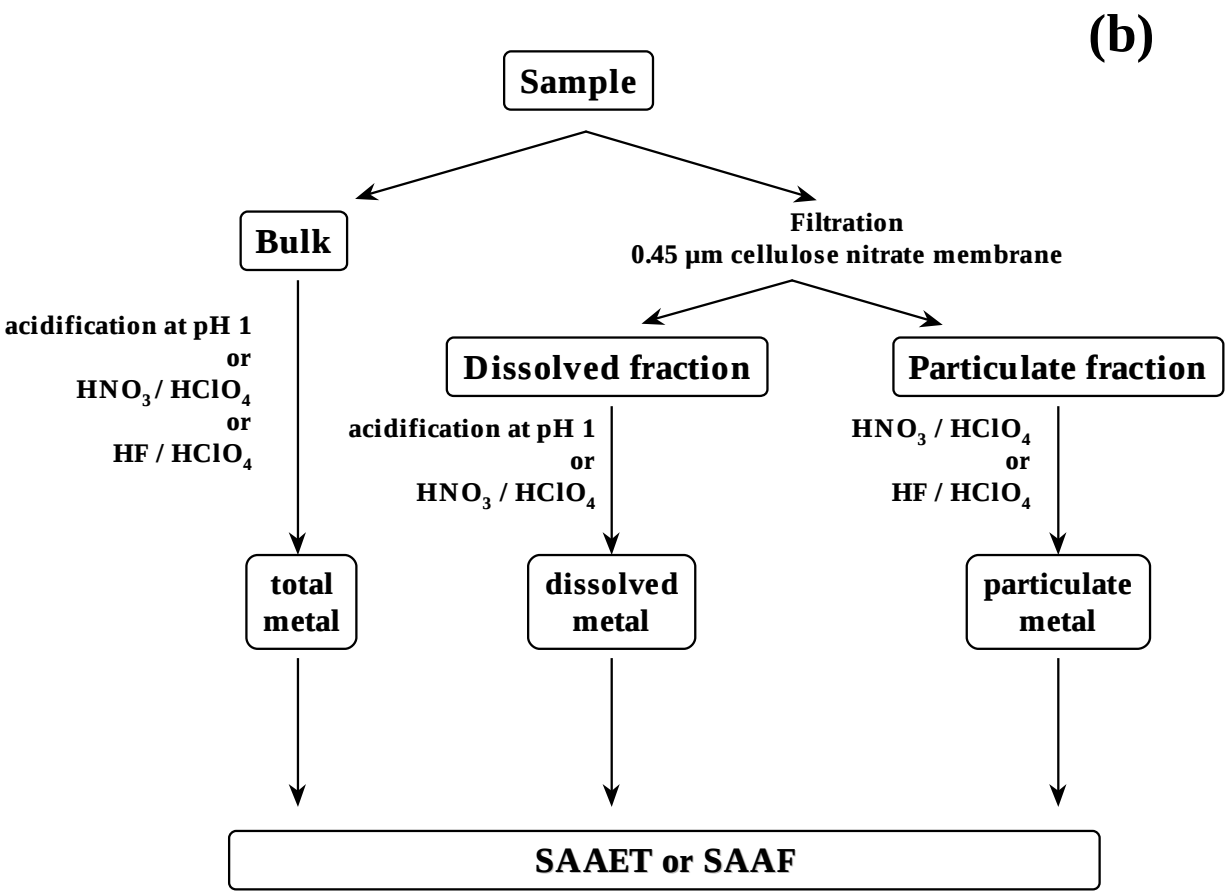


Figure 1: General scheme for (a) hydrocarbon and (b) metal determination.

The general schemes for the determination of the micropollutant are described on Figure 1. The solid phase was separated from the dissolved phase using filtration: (i) for hydrocarbons, with pre-extracted 0.45 µm membrane (Millipore), previously heated at 450°C during 2 h, (ii) for metals, with 0.45 µm cellulose nitrate membrane (Sartorius SM 11306), previously soaked in 0.5% HCl for 24 h. The solid phase was then dried to a constant weight at 40°C for hydrocarbons and 60°C for metals. Samples were kept at 4°C in the dark prior to analysis.

Determination of hydrocarbons. Aromatic and aliphatic hydrocarbons were determined by GC-MS (Hewlett Packard HP G 1800 A) using a PONA column, 50 m x 0.20 mm (Hewlett Packard). Before extraction internal perdeuterated standards were added, i.e. Dodecane D_{26}, Tetracosane D_{50}, Triacontane D_{62}, Naphtalene D_8, Phenanthrene D_{10}, Pyrene D_{10}, Benzo(a)pyrene D_{12}, Benzo(ghi)perylene D_{12}.

Determination of metals. Cd, Cu, Pb and Zn were determined by Atomic Absorption Spectroscopy (Perkin Elmer, 1100B) either in air-acetylene flame (SAAF) or in electrothermic graphite furnaces (SAAET) (Perkin Elmer, HGA 700 with AS 70 sample processor) depending on the metal concentration whatsoever the treatment of the sample was. 1 µl 100 $g.l^{-1}$ $NH_4H_2PO_4$ was added to 30-40 µl samples, as matrix modifier, for SAAET determination of cadmium and lead (Garnaud *et al.*, in press).

VALIDATION PROCEDURE OF ALIPHATIC HYDROCARBON DETERMINATION

The main problem to solve for the determination of hydrocarbons is the lack of urban samples having certified concentration in aliphatic hydrocarbons. Thus the marine sediment SRM 1941a (NIST) was used for its homogeneity and stability: it presents certified values for aromatic hydrocarbons, whereas the aliphatic concentrations are given as noncertified, i.e. indicative. Likewise, dissolved hydrocarbon extraction was assessed using a mixture of 17 dissolved aliphatic hydrocarbons (Florida TPH mix, NSI Environmental Solutions). This is the reason why the validation of the aliphatic hydrocarbons determination was considered as a priority in this work. Each step of the whole procedure has been separately investigated.

Solid-Liquid extraction of particulate hydrocarbons

Particulate samples were Soxhlet extracted for 24 h in a mixture of CH_2Cl_2/MeOH (80/20; v/v). The total organic extract was reduced to a small volume (500 µl) using a rotatory evaporator and near dryness under nitrogen stream.

Some Soxhlet blanks were analysed. Clean filters (without any particles) were introduced in a cartridge and put in the Soxhlet device. The results obtained represent 3 % of the total resolved hydrocarbons found in particulate samples from the experimental catchment "Le Marais" (Gromaire-Mertz *et al.*, 1998a, b). In order to improve these results, we isolated the Soxhlet from the laboratory atmosphere by filtering the air on top of the Soxhlet device with glass cotton. The obtained level decreased to 1% of the total resolved hydrocarbons found in particulate samples. The use of pre-combusted filters and pre-extracted cartridge gave the best blank results with 0.5 % of the total resolved hydrocarbons found in particulate samples from the experimental catchment.

The certified material SRM 1941a was used to evaluate the Soxhlet extraction efficiency. Depending upon the hydrocarbon selected, the percentage of recovery ranged between 58 and 138 %. These results, quite similar to those of Evans *et al*. (1990), i.e. 83 and 131 %, have been calculated using the indicative values given by NIST.

Liquid-Liquid extraction of dissolved hydrocarbons

The dissolved hydrocarbons were liquid-liquid extracted 4 times with 30 ml of CH_2Cl_2. The extract was then reduced to a small volume, as for the particulate samples. Different tests were performed in order to evaluate the quality of our extraction method.

A first series of blanks were carried out to test the reagents involved in the liquid-liquid extraction protocol. Perdeuterated hydrocarbons (Dodecane D_{26}, Tetracosane D_{50}, Triacontane D_{62}, Naphtalene D_8, Phenanthrene D_{10}, Pyrene D_{10}, Benzo(a)pyrene D_{12}, Benzo(ghi)perylene D_{12}) were added to the reagents as internal standards. This blank showed 6 $\mu g.l^{-1}$ of total resolved hydrocarbons which is less than 4% of the concentrations found in urban dissolved samples. We can consider our results concerning blanks as satisfying.

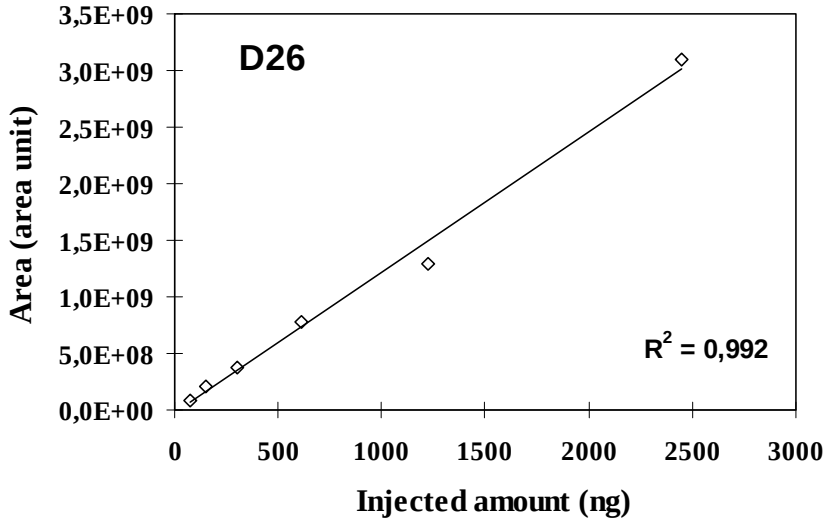
In order to evaluate the liquid-liquid extraction efficiency, we used Florida TPH mix (NSI Environmental Solutions), which is a mixture of 17 dissolved aliphatic hydrocarbons from C_{10} to C_{40}, but not an urban sample. The percentage of recovery was 96 ± 15 % (average ± standard deviation).

Use of several perdeuterated hydrocarbons for determination of aliphatic and aromatic hydrocarbons

The general scheme for hydrocarbons determination comprises an extraction step, one or several purification steps and a GC-MS quantification. During all these steps, the different analytes can be partially lost. It is therefore important to use an adequate quantification method with internal standards. The internal standard is a component which has a retention time slightly different from the retention time of the component we want to quantify. Many authors (Baumard and Budzinski, 1997b; Rogge *et al.*, 1997) chose perdeuterated hydrocarbons as internal standards.

Using GC-MS, the area of the peak is a function of the quantity injected into the analyser (Baugh, 1993). So the equation to quantify hydrocarbons can be written as follows: $C_X = C_D * A_X/A_{D,}$ with: C_X the concentration in the unknown compound, C_D the concentration of the corresponding perdeuterated compound, A_X the peak area of the unknown compound, A_D the peak area of the corresponding perdeuterated compound. Such calculations assume that sensitivities are identical for both species and that both concentrations are within the GC linear domain.

(a)



(b)

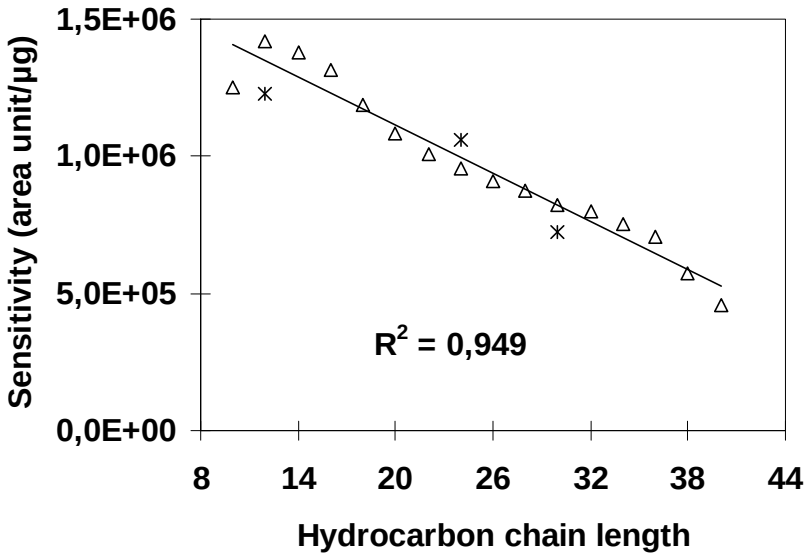


Figure 2: (a) Sensitivity determination: area of perdeuterated Dodecane D_{26} peaks *vs*. injected mass, (b) sensitivity *vs*. hydrocarbon chain length with (Δ) non perdeuterated or (*) perdeuterated hydrocarbons.

Linearity was observed between 20 and 2500 ng Dodecane D_{26} injected (Fig. 2a) and between 10 and 800 ng Tetracosane D_{50} injected, and covers the whole range of concentrations which were determined. For Triacontane D_{62}, the linearity ranged only between 50 and 800 ng injected. This limitation is probably related to the length of the carbon chain which involves lower sensitivity.

The sensitivity of a hydrocarbon analysed by GC-MS depends largely on the carbon chain length of this hydrocarbon (Barrick *et al.*, 1982) (Fig. 2b). In fact, the hydrocarbon chain length influences the hydrocarbon boiling point which itself acts on the hydrocarbon retention time. This sensitivity variation should obviously be taken into account for hydrocarbon determination. Therefore, the use of 3 different internal standards, which cover the whole range of aliphatic hydrocarbons analysed, is a good way of avoiding such errors: Dodecane D_{26} was used for hydrocarbon chain length ranging between 10 and 20, Tetracosane D_{50} between 21 and 29, and Triacontane D_{62} between 30 and 40.

Separation of aliphatic and aromatic hydrocarbons

Aliphatic hydrocarbons have to be separated from aromatic ones in order to get clearer chromatograms, for example using adsorption on silica gel (Hites *et al.*, 1980; Barrick *et al.*, 1982; Wang *et al.*, 1997). This separation was tested with a mixture of perdeuterated aliphatic (Dodecane D_{26}, Tetracosane D_{50}, and Triacontane D_{62}) and aromatic (Naphtalene D_8 -napht*-, Phenanthrene D_{10} - phe*-, Pyrene D_{10} - pyr*-, Benzo(a)pyrene D_{12}) hydrocarbons. This mixture was eluted from the silica gel column with: (i) 6 ml hexane and 6 ml of hexane-dichloromethane mixture (80:20, v/v) (method 1) or (ii) 4 ml hexane and 6 ml hexane-dichloromethane mixture (80:20, v/v) (method 2) (Fig. 3). Method 2 allows the complete separation of the aromatic compounds from the aliphatic ones. Knowing that the behaviour of a perdeuterated hydrocarbon is identical to the behaviour of the same non perdeuterated hydrocarbon, method 2 was adopted to separate aromatic hydrocarbons from aliphatic hydrocarbons.

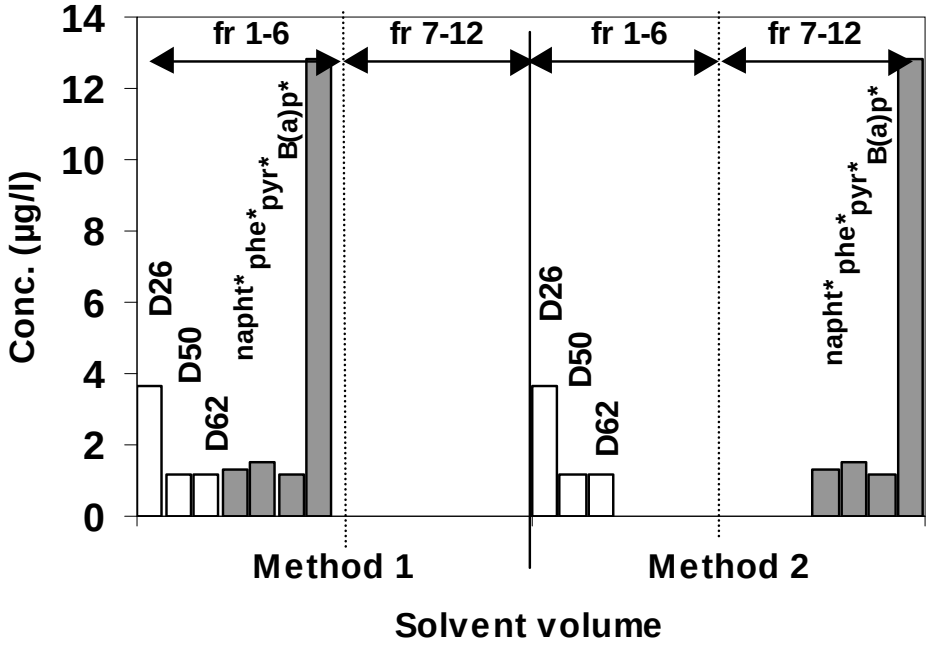


Figure 3: Comparison between two separating methods of aliphatic and aromatic hydrocarbons, using adsorption chromatography: fr i-j refers to the volume (ml) of eluting solvent and D_{26} to Dodecane, D_{50} to Tetracosane, D_{62} to Triacontane and napht* to Naphtalene D_8, phe* to Phenanthrene D_{10}, pyr* to Pyrene D_{10}, B(a)p* to Benzo(a)pyrene D_{12}.

VALIDATION PROCEDURE OF METAL DETERMINATION

Acidification or digestion for metal determination in urban samples and atmospheric deposits

Determination of dissolved metals in urban catchment samples: acidification or digestion ? The acidification at pH 1 with nitric acid gives better results than digestion using concentrated nitric-perchloric acid mixture (Fig. 4a). The digestion leads to losses of metals due to the several steps involved in the handling of the sample whereas the acidification is a one-step procedure.

Determination of particulate metals in urban catchment samples. A comparison between two types of digestion, i.e. concentrated nitric-perchloric acid mixture and fluorhydric-perchloric acid mixture, was carried out on wet and dry samples, both types of digestion yield similar metal concentration (Fig. 4b). A similar experiment, carried out on the certified sample NIST 1648 (urban particulate matter) showed the fluorhydric-perchloric digestion yield a metal amount lower than the expected amount, from 4 up to 16% (Table 1). The nitric-perchloric digestion is therefore recommended for polluted samples specially urban samples containing high amount of organic matter (Robbe, 1984; Flores-Rodriguez, 1992).

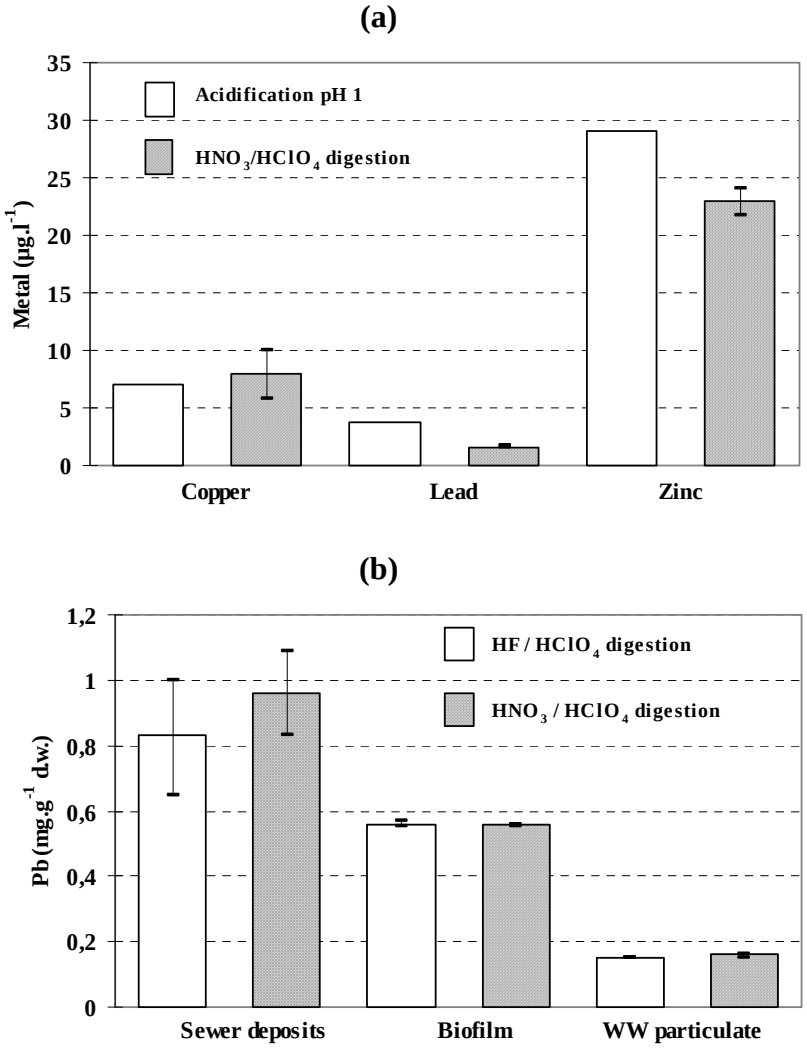


Figure 4: (a) Comparison of the dissolved metal determination using acidification at pH 1 or $HNO_3/HClO_4$ digestion, and (b) of the particulate lead determination using $HF/HClO_4$ or $HNO_3/HClO_4$ digestion.

These preliminary experiments lead us to recommend the following procedures: for dissolved metal the acidification at pH 1 with nitric acid ensures a good recovery, whereas for wet and dry samples the use of the nitric-perchloric digestion give the better results.

Table 1: Comparison between certified metal concentrations of NIST 1648 and measured concentrations using $HF\text{-}HClO_4$ and $HNO_3\text{-}HClO_4$ (mean value ± dispersion). The figure in bracket is the difference, expressed in percentage, between the measured and the certified values.

Metal	**Certified amount ($mg.kg^{-1}$ d.w.)**	**Measured amount ($mg.kg^{-1}$ d.w.)**			
		$HNO_3\text{-}HClO_4$		**$HF\text{-}HClO_4$**	
Cd	75 ± 7	84 ± 7	(+12 %)	72 ± 7	(-4 %)
Cu	609 ± 27	595 ± 23	(-2 %)	512 ± 45	(-16 %)
Pb	6550 ± 80	6460 ± 250	(-1 %)	5810 ± 390	(-11%)
Zn	4760 ± 14	5040 ± 190	(+6 %)	4310 ± 400	(-9 %)

Determination of metals in atmospheric samples. A comparison between acidification at pH 1 and nitric-perchloric digestion has been carried out on three different types of atmospheric samples: dry (n=3), wet (n=14) and bulk (n=18) deposits. Assessing dry deposition samples, pH 1 acidification leads to a recovery of only 20 to 80% of the amount extracted by digestion. On the contrary, for wet and bulk deposits,

acidification and digestion gave the same recovery. Hence those results demonstrate that the nitric-perchloric digestion was unnecessary for wet and bulk deposits, whereas it gave the best extraction for dry deposits.

The use of certified sample for dissolved and particulate metals

The nitric-perchloric digestion used for particulate metal determination was validated using 3 certified samples : NIST 1648 (urban particulate matter), BCR 144R and 146R (industrial and domestic sludge). Except for cadmium in BCR 144R sample, which levels are very low, i.e. 1.5 $mg.kg^{-1}$ d.w., deviations between measured and certified values were lower than 10 %. Whereas standard deviations obtained on replicates of particulate standard ranged between 2 to 9 %, replicates between dry deposits samples could be much worse sometimes reaching a 50 % dispersion (average dispersion was 10 %). We suggest that such large dispersion was related to a poor homogenisation of samples due to the presence of adhesive material, like soot, in the samples.

Dissolved metal determinations were also validated using 3 certified samples : NIST 1643c (fresh water), SPS WW1 and SW2 (waste and surface water). These samples were systematically used to control the validity of all calibration curves. Table 2 compares mean and standard deviation obtained with certified values and 95% limit of confidence. Except for copper in SPS SW2 sample, deviations between measured and certified values are lower than 5 %.

Table 2: Comparison between the measured and certified amounts of dissolved metal for 3 certified samples: NIST 1643, SPS WW1 and SPS SW2 (number of determinations).

Metal	**NIST 1643c ($\mu g.l^{-1}$)**		**SPS WW1 ($\mu g.l^{-1}$)**		**SPS SW2 ($\mu g.l^{-1}$)**	
	Certified	**Measured**	**Certified**	**Measured**	**Certified**	**Measured**
Cd	12.2 ± 1.0	12.0 ± 0.1 (n=20)	20.1 ± 0.1	19.6 ± 0.4 (n=9)	2.50 ± 0.01	2.53 ± 0.10 (n=9)
Cu	22.3 ± 2.8	21.6 ± 0.4 (n=23)	401 ± 2	403 ± 28 (n=16)	100 ± 1	80 ± 2 (n=11)
Pb	35.3 ± 0.9	34.4 ± 0.5 (n=23)	99.5 ± 0.5	100.1 ± 2.0 (n=9)	24.8 ± 0.1	24.0 ± 0.6 (n=9)
Zn	73.9 ± 0.9	70.0 ± 0.8 (n=32)	600 ± 10	617 ± 15 (n=32)	100 ± 1	95 ± 2 (n=20)

CONCLUSION

Urban runoff samples present a large spatial and temporal heterogeneity. It is therefore often difficult to discriminate such sample heterogeneity from the dispersion of micropollutant extraction and determination steps. Such difficulties may be solved when certified samples are available, with composition and contamination similar to actual samples. This is the case for dissolved and particulate metal present in urban samples. Digestion and metal determination procedures may be validated. Unfortunately this is not the case for metals in atmospheric deposits, either settled aerosols or rain samples: then several procedures need to be compared for their rate of extraction and repeatability. Furthermore the low level of particles within rain samples do not allow the direct determination of particulate metals: they need to be calculated from bulk and dissolved metal concentrations. The absence of urban samples certified in aliphatic hydrocarbons makes it difficult to validate the whole extraction, purification and determination procedure. It is therefore necessary to validate each step of this long procedure using either well homogenised and stabilised samples, such as SRM 1941a (marine sediment), or mixture of dissolved hydrocarbons. Addition of perdeuterated standards allows a precise determination of each detected hydrocarbon. Nevertheless, as GC sensitivity for hydrocarbon depends largely upon the length of the carbon chain, it is very important to add simultaneously at least 3 standards, covering the whole chain length range. Quality of hydrocarbon determination would greatly benefit from the availability of urban samples, both dissolved and particulate, certified for aliphatic hydrocarbons.

Acknowledgements

Authors acknowledge the support of PIREN-Seine (CNRS GDR 1067) and « Le Marais » experimental urban catchment programmes, as well as Nicole Apperry, Sylvain Lecomte, François-Jérôme Bris and Cyrille Moret for contribution.

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